INFLUENCE OF ION-EXCHANGED NICKEL ON PYROLYSIS OF LOY YANG BROWN COAL

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ABSTRACT

Influence of ion-exchanged nickel on pyrolysis of Loy Yang brown coal was examined, partly using the X-ray absorption fine structure (XAFS) technique. Pyrolysis experiments were carried out up to 1173 K at 5 K/min in helium flow. CO yields remarkably increased from 8% to 15% with increasing nickel loadings from 0 to about 3 %, whereas CO_2 yields were almost constant at about 7% in the same region of nickel contents. Above 3wt% of nickel loadings, CO and CO_2 yields gradually increased. The peak of CO evolution in the acid-washed coal, without any nickel ions, was broad at 870K. On the contrary, the peak of CO was divided into two by the loading of nickel ions. First peak, which appeared at 670-770K, shifted to lower temperature with increasing ion-exchanged nickel, while second peak appeared at about 920K independent of the amount of nickel ions. Further, by using the XAFS technique; it was shown that the nickel species aggregated to metal particles at 750K in the case of low loaded sample and that the aggregation of nickel species shifted to lower temperature by 100K at high loaded sample.

1. INTRODUCTION

The pyrolysis behavior of brown coals and lignites on heat treatment has been studied extensively.[1-3] The initial stage of pyrolysis is thought to consist of decomposition of several functional groups. The thermal decomposition of functional groups affects significantly the initial stage of coal liquefaction, gasification, and pyrolysis, where several structural changes take place simultaneously. Particularly, it is very important to understand the effects of the ion-exchanged metal species, which are associated with mainly carboxyl groups, on the decomposition process, since these cations are well known to be good catalysts for coal conversion processes. Schafer investigated the relation between the decomposition of functional groups and the evolved gas during pyrolysis of acid-washed coal and alkali or alkaline earth metal exchanged coals.[4-5] He presented that CO and CO_2, which were evolved from the acid-washed coal during heat treatment, originated from phenolic hydroxyl groups and carboxyl groups, respectively. In the case of the cation-exchanged coals, other oxygen-containing groups associated with carboxyl groups yielded CO_2 before the carboxylate groups decomposed into CO_2, that is, the presence of metal cation stabilized carboxylate groups. However, the details of the decomposition process are still not understood.

We reported previously that the temperature of the C1 gas evolution as well as the C1 gas yields during the pyrolysis of the nickel-exchanged coal changed by their loadings.[6] This result suggests that the catalytic properties depend on the structure of active species during pyrolysis. The purpose of this study is to examine the influence of ion-exchanged nickel on pyrolysis of Loy Yang brown coal, partly using the X-ray absorption fine structure (XAFS) technique, which can provide information on local structure of highly dispersed catalytic species in coal.

2. EXPERIMENATAL

2.1 Sample Preparation. Loy Yang brown coal from Victoria, Australia, was used in this study. Raw coal was ground smaller than a 250 μm particle size, washed with deionized water, dried at 323 K under vacuum, and stored in a desiccator. The analyses for this coal are as follows: C: 67.6 % (daf), H: 5.2 % (daf), N: 0.8 % (daf), O: 26.4 % (diff), and ash: 0.2 % (dry). Acid-washed coal (AW) was prepared by stirring the raw coal in 0.5 mol/l of hydrochloric acid for 24 h. The concentration of carboxyl groups was 3.7 mmol/g.[7] About 10 g of the coal sample in 500 ml of an aqueous solution of nickel chloride at a concentration of 0.1 mol/l was stirred, and the pH of the solution was adjusted by adding ammonia or hydrochloric acid. After the pH remained unchanged for 5 h, the exchange reaction was judged to be equilibrium. The extent of exchanged nickel cation was determined by extracting the cation from the sample by hydrochloric acid. The nickel cation-exchanged samples are identified by the amount of loading (wt %), e.g., 0.75Ni for 0.75 wt% nickel-exchanged coal (daf).